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1 **Catchment and in-stream influences on metal concentration and ochre deposit density**
2 **in upland streams, Northern Ireland.**

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12

13 **Abstract**

14

15 Metal concentrations from stream waters in two geological blocks in Northern Ireland were
16 compared to determine the contributions of catchment characteristics and in-stream
17 conditions. One block is composed of metamorphosed schist and unconsolidated glacial drift
18 with peat or peaty podzol (mainly humic) soils, while the other block consists of tertiary
19 basalt with brown earth and gley soils. Water samples were collected from 52 stream sites
20 and analysed for Fe, Mn and Al as well as a range of other chemical determinands known to
21 affect metal solubility. Densities of metal-rich ochre deposit were determined for stream bed
22 stone samples. Higher conductivities and concentrations of bicarbonate, alkalinity, Ca and
23 Mg occurred on basalt than on schist. Despite higher Fe and Mn oxide concentrations in
24 basalt-derived non-humic soils, stream water concentrations were much lower and ochre
25 deposit densities only one third of those on schist overlain by humic soils. Neither rock nor
26 soil type predicted Al concentrations, but pH and dissolved oxygen did. Peat-generated
27 acidity and the limited acid neutralising capacity of base-poor metamorphosed schist have
28 resulted in elevated concentrations of metals and ochre deposit in surface waters.

29

30 **Keywords**

31 Metals · Ochre deposits · Geology · Soil · pH · Dissolved oxygen

32 **Introduction**

33

34 Orange-brown deposits of iron compounds have been reported from waters in Europe (for
35 example, Åström and Åström 1997; Neal et al. 2008; Prange 2007), North America
36 (Letterman and Mitsch 1978; McKnight and Bencala 1990; Niyogi et al. 1999) and elsewhere
37 (Bray et al. 2008). Many of these are found in post-industrial landscapes and result from acid
38 mine drainage (Kimball et al. 2002; Mayes et al. 2008; Younger 2001). However, stream
39 metal deposits also occur in non-industrial, often upland, environments (Abesser et al. 2006;
40 Prange 2007), frequently resulting from drainage for farming and afforestation (Vuori 1995).
41 These deposits can have harmful effects on algae, invertebrates and fish (Vuori 1995).

42 The basic chemical processes producing ochre deposits are well known. Mobilisation
43 of Fe, Mn and Al, important components of the deposits, is influenced by bedrock
44 weathering, the presence of acidic and/or reducing conditions (Letterman and Mitsch 1978;
45 McKnight and Bencala 1990) and the concentration of dissolved organic carbon (DOC) in the
46 soil (Neal et al. 2010). Fe^{2+} and Mn^{2+} are soluble under acidic, reducing conditions, such as
47 those found in poorly buffered catchments and inadequately drained peat soils. In this state
48 these ions can be transported into receiving waterways (Abesser et al. 2006; Neal et al. 2008).
49 However, as pH increases or conditions become more oxidised in streams, they are converted
50 to insoluble Fe^{3+} and Mn^{4+} states, which precipitate onto the stream bed (Mayes et al. 2008;
51 McKnight and Bencala 1990). Aluminium chemistry in natural waters is multifaceted and
52 solubility is strongly linked to pH and complexation with humic substances (Stutter et al.
53 2001; Tipping and Carter 2011).

54 Around 90 to 95% of the Fe and Mn found in streams is derived from the surrounding
55 catchment (Durand et al. 1994; Neal et al. 1997; Rowland et al. 2012), with metal
56 concentrations increasing with increased percentage peat cover (for example, Mitchell and
57 McDonald 1995). Naturally occurring sources of catchment acidity include rainwater and
58 organic compounds, such as humic and fulvic acids (Crist et al. 1996; Paciolla et al. 2002;
59 Tipping 2002). Humic acids, and more specifically peat-moss humic acids, are reductant and
60 mobilisation agents (Neal et al. 1997; Paciolla et al. 2002; Rothwell et al. 2008). For
61 example, in the upper River Severn catchment in mid-Wales, Fe is mainly catchment-derived
62 and the highest concentrations were observed under reducing conditions. Stream water Fe
63 concentrations in the catchment have doubled in the last 20 years and are strongly correlated
64 with a rise in soil DOC concentrations (Neal et al. 2008): peat is a major source of DOC

65 (Hope et al. 1997). Increased Al concentrations in upland catchments are associated with
66 conifer plantation forestry (Grieve and Marsden 2001; Neal et al. 2010).

67 Upland catchments in the British Isles tend to experience high annual rainfall as
68 maximum precipitation often occurs at the highest altitudes (Betts 1997; Burt and Ferranti
69 2012; Hudson et al. 1997) and leaching becomes important where rainfall exceeds
70 evapotranspiration, particularly at altitudes greater than 250 m (Cruickshank 1997; Neal et al.
71 2010). Catchment geomorphology can strongly influence headwater discharge and chemistry,
72 particularly that of Fe, Mn and DOC (Clark et al. 2008; Neal et al. 2010; Worrall et al. 2006).
73 In upland catchments two distinct sources of Fe and Mn have been identified: organic
74 soilwater and deep soilwater/groundwater (Abesser et al. 2006). The relative contribution of
75 these sources is dependent upon antecedent conditions and storm event magnitude. Metals
76 from organic soilwater tended to dominate during storm events, whereas deep
77 soilwater/groundwater sources were important during periods of low flow (Abesser et al.
78 2006; Neal et al. 2010). Acidic conditions prevail in headwaters due to the dominance of peat
79 soils with their limited acid neutralising capacity (ANC).

80 In this study, the role of catchment geology (basalt versus schist and unconsolidated
81 drift) and soil type (humic versus non-humic) on stream water metal concentrations and ochre
82 deposit densities was investigated as part of wider research aimed at determining the
83 ecological effects of ochre deposition on upland stream ecology. Here we document the
84 catchment characteristics and in-stream conditions that potentially determine high metal
85 concentrations and deposit densities in stream systems in two geologically distinct blocks of
86 Northern Ireland. The paper examines a) the influence of geology and soil type on stream
87 metal concentrations and b) the role of stream water pH and dissolved oxygen (DO) on metal
88 solubility.

89

90 **Study area**

91

92 Bazley (1997) recognised four major geological blocks in Northern Ireland. The Sperrin
93 Mountains form part of the oldest block, of acidic, base-poor, metamorphosed schist,
94 unconsolidated glacial drift and alluvium, while the youngest block, which includes the
95 Antrim plateau, is formed from volcanic lavas and is primarily tertiary basalt (Fig. 1).

96 Brown earth, podzol, surface water gley, humic ranker, organic alluvium, peat, peaty
97 podzol, surface water humic gley soil types were found in the study site catchments, the last
98 five of which were categorised as humic soils for statistical analysis purposes. Soils in the

99 Sperrin Mountains are predominantly peat or peaty podzol (Cruickshank 1997; Mitchell
100 2004) and extensive areas of bog and moorland dominate slopes. Antrim Plateau soils are
101 mainly brown earths and gleys (Cruickshank 1997).

102 Climatic conditions in Northern Ireland are mostly wet and mild as a consequence of
103 a mid-latitude position and the influence of the North Atlantic Drift (Betts 1997). Upland
104 areas receive the highest annual precipitation and there is a progressive decline in rainfall
105 levels across the province from west to east. The Sperrin Mountains receive in excess of 1600
106 mm annually, compared with less than 1300 mm in the Antrim Plateau (Betts 1997).

107

108 **Materials and methods**

109

110 **Sampling and laboratory analysis**

111

112 Stream water and ochre deposit samples were collected from 52 sites, 35 in the Sperrin
113 Mountains and 17 in the Antrim Plateau in April 2007 (Fig. 1). The study sites, on small (1–2
114 m wide) upland streams, were chosen because of differing geology, soil type, accessibility
115 and lack of human interference. Ordnance Survey of Northern Ireland topographical and soil
116 maps (1:50,000) were used to determine altitude, gradient, soil and rock (soil substrate) type.
117 Rock substrates were categorised as basalt and schist/unconsolidated drift, and soils as humic
118 or non-humic. Stream gradient was calculated from elevation changes across contour lines in
119 metres per metre and expressed as a percentage.

120 Stream water was analysed, *in situ*, for DO, temperature, conductivity and pH. A
121 HACH HQ 10 portable meter with LDO probe was used to measure DO (% saturation) and
122 temperature (°C). A HACH *sensION*TM156 portable meter was used to measure conductivity
123 ($\mu\text{S cm}^{-1}$) and pH. Probes were calibrated prior to sampling in accordance with HACH
124 operation manuals. Water samples were collected for dissolved and particulate chemical
125 determinants in clean, 250 ml polypropylene bottles. Bottles were pre-acidified with 2 ml (\pm
126 0.1) of 5 M hydrochloric acid per 100 ml of sample to prevent the precipitation and/or
127 sorption of metals. Samples were taken from the centre of the stream channel at
128 approximately 5 cm below the water surface.

129 Total, soluble and particulate fractions were determined (in the laboratory) for Fe,
130 Mn, and Al; only total values are presented as all fractions were strongly correlated. Fe, Mn
131 and Al concentrations were determined by spectrometry using 2, 4, 6-tripyridyl-1, 3, 5-

132 triazine, formaldoxime and pyrocatechol violet respectively (HMSO 1978a; 1978b; 1980).
133 Acid digestion was performed on unfiltered samples according to Eisenreich et al. (1975).
134 Blanks (Millipore Milli-Q) and standards were included, in triplicate, for each chemical
135 determinand.

136 Ochre deposit material on the upper surface of two to five stones was removed by
137 spatula, brush and rinsing with Millipore Milli-Q grade water. This material was oven dried
138 at 65 °C until there was no further weight loss. Deposit density was calculated as the mass of
139 material per unit surface area: the latter was determined by covering the upper stone surface
140 with aluminium foil, which was weighed and converted to area.

141

142 Tellus Project data

143

144 Geochemical data for each of the 52 sites was obtained from the Geological Survey of
145 Northern Ireland Tellus Project. The Tellus project collected soil samples at regular grid
146 intervals of one site per 2 km² and stream water samples at an average of one site per 2 km²,
147 over the whole land surface of Northern Ireland. Elements and inorganic compounds were
148 analysed using X-ray fluorescence, ion chromatography and inductively coupled plasma
149 (ICP) mass spectrometry. Soil parameters used in this paper were: pH; Calcium (Ca);
150 Magnesium (Mg); Fe and Mn oxide. Water parameters were: pH; conductivity; bicarbonate;
151 alkalinity; Ca; Mg; Fe; Mn; Al and DOC. Tellus data were collected at a different spatial
152 scale and on different dates from our samples, so as a check on comparability correlations
153 between variables measured in common were calculated (conductivity, pH, Fe, Mn, Al): the
154 correlation for Al was not significant ($r = 0.20$) but those for the other variables were ($r =$
155 $0.75 - 0.86$, $n = 50$, $P < 0.001$).

156

157 Statistical analysis

158

159 Data were tested for normality and with the exception of altitude, pH, DO and temperature,
160 variables were log₁₀ transformed: all statistical tests use the transformed data. Relationships
161 between the catchment and stream variables were explored by principal component analysis
162 (PCA), with varimax rotation. Differences between the Sperrin Mountain and Antrim Plateau
163 sites were determined by discriminant analysis; linear regression; general linear modelling
164 (GLM) and analysis of covariance (ANCOVA). Statistical analysis and graphical outputs
165 were generated using the SYSTAT 13 statistical software package.

166

167 **Results**

168

169 Physical and chemical characteristics of the 52 study sites (surveyed in 2007) are summarised
170 in Table 1a. The majority (83%) of streams in the Sperrin Mountains drain catchments with
171 humic soils overlying schist and unconsolidated drift, whereas on the Antrim Plateau, the
172 dominant rock type is basalt and there is not a preponderance of humic soils (Table 1b).
173 There were significant differences between geological blocks in DO, temperature, pH,
174 conductivity, Fe, Mn and Al. As expected from the geology and soils, stream water
175 conductivity and pH were higher and Fe, Mn and Al concentrations lower on the Antrim
176 Plateau. These differences are reflected in ochre deposit densities, which were significantly
177 greater in the Sperrin Mountains (medians 6.68, 2.06 mg cm⁻², $P < 0.01$) (Fig 2). Discriminant
178 analysis correctly allocated all but one of the 52 sites to rock type, by conductivity, pH and
179 altitude. Humic soils occurred at significantly higher altitudes than non-humic soils (means
180 260, 194 m, $F_{1,49} = 28.08$, $P < 0.001$), but there was no difference across blocks.

181 All the soil (pH; Ca; Mg; Fe; Mn) and water (pH; conductivity; bicarbonate;
182 alkalinity; Ca; Mg; Fe; Mn; Al; DOC) determinands measured by the Tellus Project (Table
183 2) differed significantly across rock type. Conductivity and base ion concentrations were two
184 and four times higher for streams located on basalt, as expected from the geology. Soils
185 overlying basalt contained more Fe and Mn than those over schist/unconsolidated drift, yet
186 concentrations of Fe and Mn in stream water were only 27% and 10% of those in the poorly
187 buffered schist sites. Water Fe concentrations increased with DOC in both geological blocks
188 (schist/unconsolidated drift $r = 0.46$, $n = 31$, $P < 0.01$; basalt $r = 0.77$, $n = 18$, $P < 0.001$).
189 However, while DOC concentrations on basalt tended to be 39% higher,
190 schist/unconsolidated drift sites had 4.0 times the Fe concentrations for a given DOC value
191 (slopes $F_{1,45} = 1.20$, $P > 0.2$; intercepts $F_{1,46} = 72.92$, $P < 0.001$): elevated Fe concentrations in
192 schist/unconsolidated drift streams (Table 2) suggest that DOC does not control Fe
193 mobilisation in this geological block.

194 Across all sites, metal concentrations in the 2007 stream water survey were negatively
195 correlated with pH and DO on the first PCA axis, temperature and conductivity with the
196 second axis, while altitude and stream gradient were aligned with the third axis (Table 3a).
197 These relationships were similar in both geological blocks. PCAs of the Tellus Project stream
198 water data (Table 3b) were also consistent across rock type ($r = 0.90, 0.88$, $P \leq 0.001$)

199 respectively), with the first axis varying with base content/acid neutralising capacity and the
200 second with pH, Fe and Mn concentrations. Note that Al is more strongly associated with the
201 first axis.

202 Rock type and soil humic content affected the concentrations of Fe and Mn in stream
203 water, but had no effect on Al concentrations (Table 4). Streams draining basalt areas had
204 only 40% of the Fe and 45% of the Mn concentrations of schist/unconsolidated drift, while
205 streams draining humic soils had higher Fe and Mn concentrations than those from non-
206 humic soils, by factors of 1.97 and 1.85 respectively. DO levels and pH negatively affected
207 the concentration of all three metals, particularly Al, in stream water (DO effect for Mn, $P =$
208 0.06). Ochre deposit density was also negatively correlated with DO and pH ($r = -0.48, -0.49,$
209 $n = 50, P < 0.001$).

210

211 Discussion

212

213 Anthropogenic influences on the study sites are limited, with only low intensity sheep
214 farming and localised conifer plantation forestry: there is no evidence of mining occurring
215 now or in the past in the study catchments. Hence the geochemical differences that exist
216 between sites reflect variations in catchment geology, soils, topography and climate.

217 Despite our survey data and the Tellus Project data being collected at different times
218 and different spatial resolution, four of the five determinands common to both datasets were
219 correlated across all sites. In addition to this both datasets showed lower Fe and Mn
220 concentrations in stream waters draining basalt. The differential in stream water
221 concentrations across rock types was somewhat different (Fe 27%, 40%; Mn 10%, 45% for
222 Tellus project and the 2007 data respectively), but this could simply reflect variations in
223 rainfall levels and throughflow volumes when the samples were collected.

224 In the literature, concentrations of major ions in stream water are highly correlated
225 with bedrock geology and soil weathering (Robson and Neal 1997; Smart et al. 1998;
226 Thornton and Dise 1998). Basalt is rich in calcium, magnesium and iron oxides (Lutgens and
227 Tarbuck 2008) and the associated soils are characterised by high base status and ANC that
228 maintain circumneutral pH and high electrical conductivities in surface waters. All soil types
229 analysed in this study were acidic (3.0-5.1): median soil pH for sites located on basalt was
230 4.39 compared to 3.43 on schist/unconsolidated drift, a difference of 0.96 pH units. Prange
231 (2007) noted that oxidation of Fe^{2+} to Fe^{3+} is accelerated by a factor of 100 if the pH is raised
232 by one unit. Consequently, higher ANC and less acidic soils on basalt geology reduces metal

233 solubility and mobilisation compared to schist/unconsolidated drift. Peat and the limited ANC
234 of base-poor schist has led to acidic conditions and elevated Fe and Mn concentrations in
235 surface waters.

236 In addition, the predominantly schist dominated Sperrin Mountains, receive more
237 rainfall per annum compared to the basalt rich Antrim Plateau (Cruickshank 1997), which
238 increases the likelihood of metal transport from the catchment. Al concentrations in this study
239 did not differ across rock or soil type, but were more closely associated with pH and DO.
240 Forests are known to increase Al concentrations in catchments as they actively scavenge
241 acidic oxides from the air (Neal et al. 2010), but few forested areas are present in either
242 geological block: hence variations in Al concentration are more likely to reflect differing
243 stream water conditions.

244

245 **Conclusion**

246

247 Multiple chemical and biological factors are known to control metal solubility: pH; DO;
248 redox potential; complexing by organic ligands; DOC; presence of ferromanganese
249 depositing bacteria. In this study, catchment and in-stream factors influencing metal
250 concentration and ochre deposit density have been investigated across contrasting geological
251 blocks. Soil type has been highlighted as an important variable in the supply and release of
252 metals from catchments to upland surface waters. Concentrations of Fe and DOC increase in
253 tandem in surface waters as both are largely catchment derived. Stream water metal
254 concentrations decrease with increasing pH and DO. As conditions become more oxidised
255 and pH increases, metal solubility decreases, and ochraceous material precipitates onto the
256 stream bed. The effects and implications of rising metal concentrations and ochre deposition
257 in aqueous systems is well documented in the context of acid mine drainage. Nevertheless,
258 research into naturally occurring instances of high stream metal and deposit concentrations is
259 necessary to provide base-line information for non-industrial catchments.

260

261

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263

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273

274 **References**

275

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386
387

388 **Figure Captions**

389

390 **Fig. 1** Topographic map showing the location of the 52 study sites (black dots) within
391 Northern Ireland. The thick solid lines delimit the four geological blocks identified by Bazley
392 (1997)

393

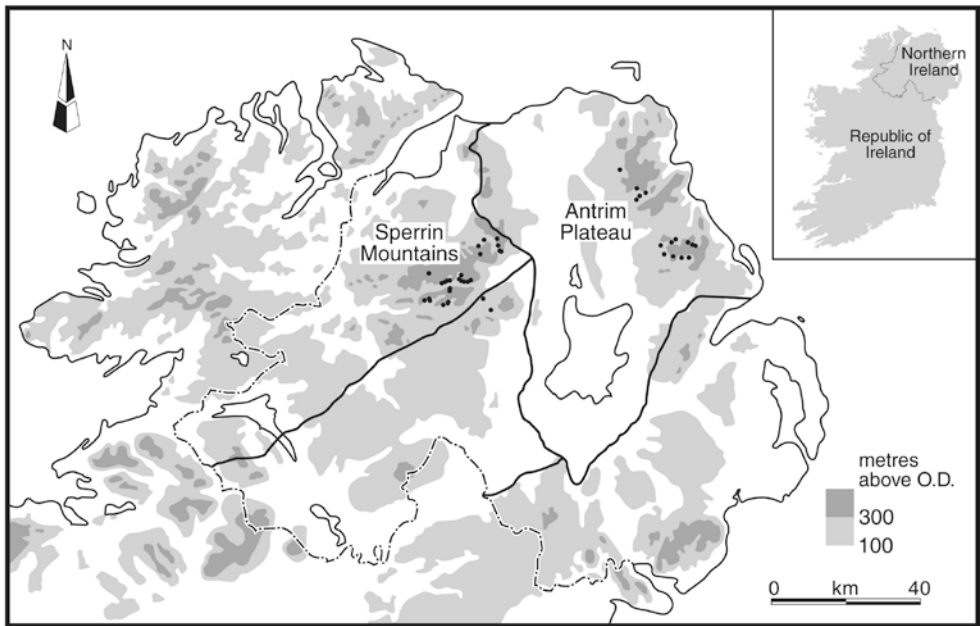
394 **Fig. 2** Histograms showing the concentrations (mg cm^{-2}) of ochraceous deposits on stones in
395 the Antrim Plateau: basalt; non-humic soil (dark shading) and Sperrin Mountains: schist;
396 humic soil (light shading)

397

398 **Figures**

399

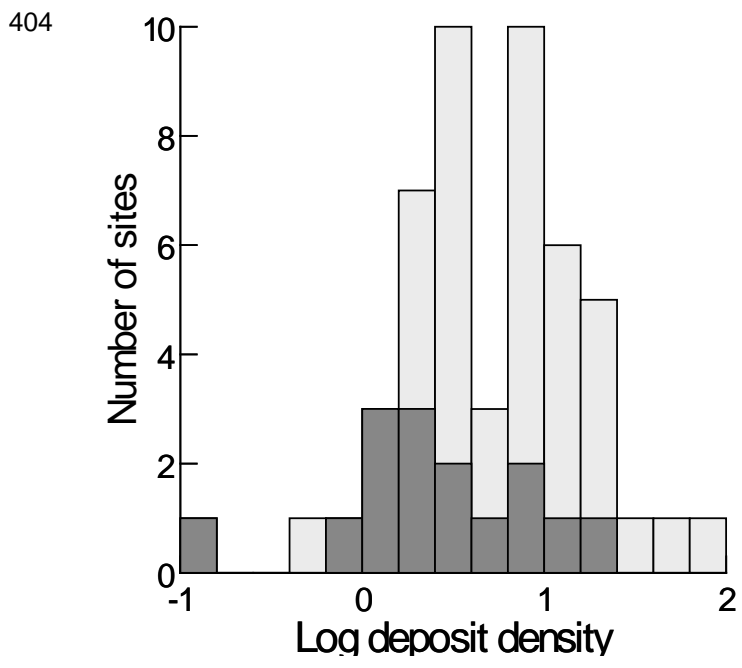
400 **Fig. 1**



401

402

403 **Fig. 2**



405 **Table 1** (a) Summary of the physical and chemical characteristics of the 52 streams surveyed
 406 in 2007 and (b) distribution of soil and rock types in the catchments of the streams sampled.
 407 Differences in the medians between geological blocks were tested using the Mann-Whitney
 408 test

409
 410 (a)

	Sperrin sites (<i>n</i> = 35)			Antrim sites (<i>n</i> = 17)			
	Minimum	Maximum	Median	Minimum	Maximum	Median	
Altitude (m)	175	360	235	155	305	240	
Gradient (%)	0.59	10.00	3.64	0.80	6.67	2.86	
% DO	55	111	101	*	76	118	104
Temperature (°C)	6.0	11.9	9.4	**	6.2	10.8	7.7
pH	6.3	7.8	7.4	***	6.8	8.6	8.0
Conductivity (µS cm ⁻¹)	65	258	94	***	220	351	273
Fe (mg L ⁻¹)	0.011	10.772	1.408	***	0.052	9.887	0.253
Mn (mg L ⁻¹)	0.023	1.590	0.390	***	0.038	0.720	0.105
Al (mg L ⁻¹)	0.018	0.939	0.086	**	0.018	0.465	0.030

411 **P*<0.05, ***P*<0.01, ****P*<0.001

412

413 (b)

	Basalt	Gravel	Alluvium	Schist	⁴¹⁴ Total
Sperrin sites					
Humic soils	1	2	14	12	29
Non-humic soils	1	4	0	1	6
Total	2	6	14	13	35
Antrim sites					
Humic soils	8	0	1	0	9
Non-humic soils	8	0	0	0	8
Total	16	0	1	0	17

415

416

417 **Table 2** Tellus Project data median soil and stream water parameters for the 52 sample sites
 418 and the ratios between schist/unconsolidated drift:basalt rocks. All values are significantly
 419 different between rock-type (Mann-Whitney test, $P<0.05$)

420

	Schist/unconsol. drift	Basalt	Ratio
Soil			
pH	3.43	4.39	1.28
Ca oxide (%)	0.57	1.56	2.73
Mg oxide (%)	0.80	1.29	1.62
Fe oxide (%)	2.05	5.32	2.60
Mn oxide (%)	0.03	0.08	3.37
Water			
pH	7.10	7.92	1.12
Conductivity ($\mu\text{S cm}^{-1}$)	72.95	167.88	2.30
Bicarbonate (mg L^{-1})	20.65	93.97	4.55
Alkalinity (mg L^{-1})	20.14	76.91	3.82
Ca (mg L^{-1})	5.20	16.48	3.17
Mg (mg L^{-1})	2.21	10.91	4.93
Fe (mg L^{-1})	1.43	0.38	0.27
Mn (mg L^{-1})	213.80	20.56	0.10
Al (mg L^{-1})	101.62	83.95	0.83
DOC (mg L^{-1})	11.12	15.42	1.39

421

422

423 **Table 3** Varimax-rotated PCA component loadings for (a) the 2007 survey data across all
 424 sites and (b) the Tellus Project stream water data for each rock type. Significant loadings are
 425 shown in bold

426

427 (a)

	Factor 1	Factor 2	Factor 3
Altitude	0.15	-0.39	0.77
Gradient	-0.22	0.23	0.69
DO	-0.73	0.12	0.24
Temperature	0.03	0.89	-0.13
pH	-0.84	-0.13	0.18
Conductivity	-0.40	-0.76	-0.16
Fe	0.91	0.22	0.02
Mn	0.87	0.27	0.18
Al	0.93	0.05	0.03
% variance	43	19	14

428

429

430 (b)

	Schist/unconsol. drift		Basalt	
	Factor 1	Factor 2	Factor 1	Factor 2
Conductivity	0.64	0.14	0.95	0.30
Bicarbonate	0.88	0.30	0.93	0.34
Alkalinity	0.41	-0.38	0.93	0.34
Ca	0.89	0.21	0.93	0.33
Mg	0.87	0.31	0.94	0.27
pH	0.38	0.76	0.60	0.63
Fe	-0.18	-0.83	-0.41	-0.81
Mn	-0.24	-0.77	0.04	-0.96
Al	-0.55	0.24	-0.93	-0.05
DOC	0.14	-0.77	-0.46	-0.71
% variance	35	29	60	30

431

432

433 **Table 4** (a) GLM results for catchment rock and soil type effects on the (\log_{10})
 434 concentrations of Fe, Mn and Al in stream waters in the 2007 survey and (b) least squares
 435 adjusted means

436

437 (a)

Source	Fe			Mn			Al		
	df	MS	<i>F</i>	df	MS	<i>F</i>	df	MS	<i>F</i>
Rock type	1	0.905	11.30**	1	0.737	15.54***	1	0.088	1.77
Soil humic content	1	0.719	8.98**	1	0.624	13.15***	1	0.125	2.51
DO	1	0.450	5.62*	1	0.174	3.67	1	0.536	10.75**
pH	1	0.392	4.90*	1	0.217	4.57*	1	0.410	8.22**
Error	45	0.080		46	0.047		45	0.050	
<i>R</i> ²		0.73			0.73			0.68	

438 **P*<0.05, ***P*<0.01, ****P*<0.001

439

440 (b)

441 Least squares adjusted means

	Fe		Mn		Al	
	Mean±se	<i>n</i>	Mean±se	<i>n</i>	Mean±se	<i>n</i>
Basalt	-0.421±0.086	17	-0.860±0.062	18	-1.320±0.063	18
Schist/unconsol. drift	-0.024±0.065	33	-0.517±0.050	33	-1.201±0.052	32
Humic	-0.076±0.053	37	-0.555±0.041	37	-1.321±0.061	36
Non-humic	-0.370±0.081	13	-0.823±0.059	14	-1.200±0.042	14

442